

Communications to the Editor

Nonplanar Structures of Cyclobutadiene Dications

Sir:

Olah and coworkers have prepared a number of methyl, phenyl, and fluorine substituted cyclobutadiene dications in superacid media, but little detailed structural information is available.¹ The parent dication is not yet known in solution although $C_4H_4^{2+}$ species of undetermined structure may have been encountered in the gas phase.² Hückel molecular orbital theory predicts the aromatically stabilized 2π -electron cyclobutadiene dication to possess a square-planar (D_{4h}) ground-state geometry (I). The resulting conclusions concerning the planarity of I, although widely held or implicitly assumed,^{1,3} apparently *have never been subjected to critical examination*. We present here the results of ab initio molecular orbital calculations which suggest that the parent cyclobutadiene dication, as well as the tetramethyl derivative,^{1a} is not planar, but prefers rather strongly puckered geometries (II and IV) instead.

The cyclobutadiene dication geometry was optimized within two overall molecular symmetry constraints, D_{4h} (I) and D_{2d} (II), using the Gaussian 70 series of programs^{4a} and three basis sets, minimal STO-3G,^{4b} split valence 4-31G,^{4c} and a basis set containing a split valence as well as polarization functions on carbon, 6-31G*.^{4d} The C_1-C_2 and C-H bond lengths of I were chosen for optimization. In II, with four geometrical degrees of freedom, the optimization also included the puckering amplitude, q , which measures the distance between the two C-C diagonals, as well as the hydrogen tilt angle, α , between a C-H bond and the $C_\beta CC_\beta$ bisector. All parameters were optimized simultaneously with a procedure^{5a} based on the conjugate gradient scheme of Davidon, Fletcher, and Powell.^{5b}

At all calculational levels, II was the lowest energy structure for the cyclobutadiene dication. The calculated barrier to inversion through the D_{4h} form (I) increases in the restricted Hartree-Fock (RHF) approximation with improvement in the basis set, from 2.8 kcal/mol at RHF/STO-3G and 4.6 kcal/mol at RHF/4-31G to 7.5 kcal/mol at RHF/6-31G* using the optimized geometries.^{6a} The optimized values for the geometrical parameters in the planar form (I) follow: $R(C_1-C_2) = 1.467$ and $R(C-H) = 1.119$ Å (RHF/STO-3G); $R(C_1-C_2) = 1.442$ and $R(C-H) = 1.077$ Å (RHF/4-31G);^{3b} $R(C_1-C_2) = 1.432$ and $R(C-H) = 1.083$ Å (RHF/6-31G*). In the puckered structure we obtain $R(C_1-C_2) = 1.457$ Å, $R(C-H) = 1.120$ Å, $q = 0.301$ Å, $\alpha = 2.7^\circ$ (RHF/STO-3G); at RHF/4-31G, $R(C_1-C_2) = 1.431$ Å, $R(C-H) = 1.077$ Å, $q = 0.318$ Å, $\alpha = 1.5^\circ$; and at RHF/6-31G*, $R(C_1-C_2) = 1.414$ Å, $R(C-H) = 1.084$ Å, $q = 0.376$ Å, $\alpha = 1.6^\circ$. These values correspond to dihedral angles between the CCC planes in II of 146.8° (RHF/STO-3G), 144.2° (RHF/4-31G) and 137.4° (RHF/6-31G*). As shown in II, the hydrogens prefer to move to *axial* positions. Distortions toward various alternative D_{2h} and C_{2v} structures led to immediate increases in total energy, and no minimum on the potential energy surface other than II could be located. I was a saddle point for planar inversion.

Several authors have discussed in detail the structural and energetic effects of 1,3 interactions in four-membered rings, notably in cyclobutane,⁷ Alleviation of these antibonding, destabilizing interactions exert a major driving force for

Table I. Orbital Energies ϵ (au) of Planar (I) and Puckered (II) Cyclobutadiene Dications (RHF/STO-3G).

I, D_{4h}		II, D_{2d}		Difference, $\epsilon(I - II)$
Orbital	ϵ	Orbital	ϵ	
$1e_g$	-0.4402 (LUMO)	$4e$	-0.4141 (LUMO)	-0.0261
$1a_{2u}(\pi)$	-0.9679 (HOMO)	$3b_2$	-0.9691 (HOMO)	+0.0012
$3e_u$	-1.0496	$3e$	-1.0670	+0.0174
$1b_{1g}$	-1.1020	$1b_1$	-1.0962	-0.0058
$2b_{2g}$	-1.1990	$2b_2$	-1.2153 ^a	+0.0163
$3a_{1g}$	-1.2155	$3a_1$	-1.2155 ^a	0.0000
$2e_u$	-1.4041	$2e$	-1.4051	+0.0010
$2a_{1g}$	-1.7488	$2a_1$	-1.7747	+0.0259

^a At RHF/6-31G*, the $2b_2$ orbital is lower in energy than the $3a_1$.

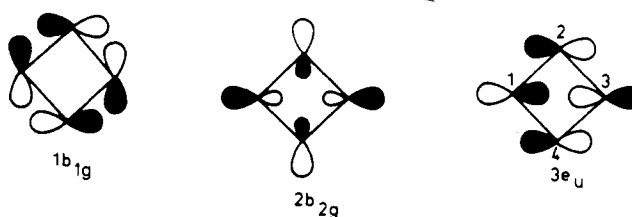
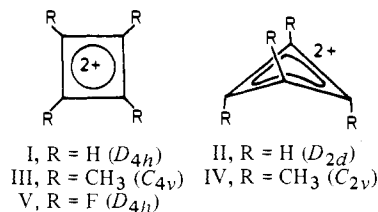


Figure 1. Schematic representation of the $1b_{1g}$, the $2b_{2g}$, and one of the $3e_u$ molecular orbitals.



puckering of the cyclobutadiene dication as well, although the concomitant changes in molecular geometry and symmetry also are important. The energetic advantages arising from puckering are clearly reflected in the energies of the valence molecular orbitals (Table I). The decrease in symmetry from D_{4h} to D_{2d} allows greater mixing among the orbitals; in particular, the D_{4h} b_{1u} and e_g symmetry representations, which are only found among the virtual orbitals, transform in D_{2d} into a_1 and e which are well represented among the occupied MO's. Only one occupied valence orbital is strongly destabilized in the D_{2d} conformation relative to the D_{4h} conformation, namely the $1b_{1g}$ orbital which is the 1,2-bonding, 1,3-antibonding Walsh-type ring orbital of p_x and p_y character (Figure 1).⁷ The major stabilization on going from D_{4h} to D_{2d} occurs in the $3e_u$, $2b_{2g}$, and $2a_{1g}$ orbitals. The last is mostly composed of C_{2s} orbitals and is lowered primarily through enhanced overlap in the D_{2d} geometry (II), in which the C_1-C_2 and C_1-C_3 distances are shortened by 0.02 and 0.09 Å, respectively, relative to those in I (RHF/6-31G*). In both the $2b_{2g}$ and $3e_u$ orbitals, the C-H bond back lobes point toward each other inside the ring (Figure 1). In the $2b_{2g}$ orbital two nodal planes bisect the C-C bonds, resulting in an absence of electron density in the center of the ring. Puckering forces the orbitals out of plane, and 1,3 bonding develops pairwise between the back lobes. The stabilization is so large that the $2b_2$ orbital energy drops below

the $3a_1$ (RHF/6-31G*). The degenerate $3e_u$ orbitals (Figure 1) are strongly 1,3 antibonding. Puckering decreases this 1,3 antibonding by tilting the hybrid orbitals and reducing their overlap. This effect also results from strong mixing with the LUMO e_g (D_{4h}) set of p_z orbitals upon distortion and is enhanced by the slight bending of the hydrogens.

The change in 1,3 bonding also manifests itself in the Mulliken electronic population analysis.⁸ The total C_1 - C_3 overlap populations in I are large and negative, -0.359 (RHF/6-31G*), whereas in II the 1,3 interaction is indicated to be weakly bonding (C_1 - C_3 overlap population = $+0.076$).

It is an oversimplification to attribute the puckering of the cyclobutadiene dication to any single effect. Nevertheless, part of the destabilizing 1,3 interactions in a four-membered ring may be relieved through puckering, and this geometrical alteration occurs despite the expected loss of resonance energy⁹ and the increase in angle strain. Orbital mixing and orbital reorientation, enhanced through pyramidalization, stabilize the puckered form. This interplay of effects seems to be fairly general and is to be found in isoelectronic four-membered ring systems containing boron as well.¹⁰ Substituents may change the preferred conformation; the strong donation of π electrons to the ring indicated by the NMR data¹ suggests that planar substituted cyclobutadiene dications may also be found. Indeed, the tetrafluorocyclobutadiene dication is indicated (RHF/STO-3G) to be planar (V).^{11a} However, the tetramethyl species, known experimentally,^{1a} is calculated to be more stable puckered (IV)^{11c} than planar (III).^{11b} The RHF/STO-3G difference, 2.3 kcal/mol, is not much smaller than that for the unsubstituted species (I vs. II). Higher level calculations on III and IV, although not yet feasible, would probably also indicate a larger difference. This suggests the possibility of experimental verification of these predictions.¹²⁻¹⁴

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References and Notes

- (1) For experimental findings and reviews of the literature, see (a) G. A. Olah and J. S. Staral, *J. Am. Chem. Soc.*, **98**, 6290 (1976); (b) G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970); (c) G. A. Olah, J. M. Bollinger, and A. M. White, *ibid.*, **91**, 3667 (1969); (d) P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971, pp 82, 83; (e) J. P. Snyder, Ed., "Nonbenzenoid Aromatics", Vol. II, Academic Press, New York, N.Y., 1971, pp 260-262; (f) G. M. Badger, "Aromatic Character and Aromaticity", Cambridge University Press, Cambridge, 1969, pp 76-77; (g) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967, pp 122-127; (h) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960), and ref 24, cited therein.
- (2) J. H. Beynon, A. Mathias, and A. E. Williams, *Org. Mass. Spectrom.*, **5**, 303 (1971); W. J. Hehre, private communication. The cyclobutadiene dication may not be the most stable isomer of $C_4H_4^{2+}$. At the 4-31G optimized level, perpendicular $H_2C^+C\equiv CCH_2^+$ (D_{2d}) with $R(C_1-C_2) = 1.339$ Å, $R(C_2-C_3) = 1.251$ Å, $R(C-H) = 1.087$ Å, $HCC = 120.7^\circ$, has an energy of -152.68366 au, some 11.7 kcal/mol more stable than the cyclobutadiene dication at the same level. For a discussion of possible dissociation into monocation fragments, see ref 3b.
- (3) (a) C. U. Pittman, Jr., A. Kress, and L. D. Kispert, *J. Org. Chem.*, **39**, 378 (1974); (b) L. Radom and H. F. Schaefer III, *J. Am. Chem. Soc.*, **99**, 7522 (1977); (c) M. J. S. Dewar and M. L. McKee, *ibid.*, in press. We thank Professor Dewar for a preprint of this paper.
- (4) (a) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, QCPE, Indiana University; (b) W. J. Hehre, R. P. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (c) W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4253 (1972); (d) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
- (5) (a) D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975); (b) W. C. Davidson, *Comput. J.*, **10**, 406 (1968); R. Fletcher and M. J. D. Powell, *ibid.*, **6**, 163 (1963).
- (6) The total energies (in au) follow: for the D_{4h} conformation (I), $E(\text{STO-3G}) = -151.08124$, $E(4-31G) = -152.65773$, and $E(6-31G^*) = -152.90451$; for the D_{2d} conformation (II), $E(\text{STO-3G}) = -151.08576$, $E(4-31G) = -152.66498$, and $E(6-31G^*) = -152.91650$.
- (7) (a) J. D. Dunitz and V. Shomaker, *J. Chem. Phys.*, **20**, 1703 (1952). (b) J. S. Wright and L. Salem, *J. Am. Chem. Soc.*, **94**, 322 (1972); L. Salem, *Chem. Br.*, **5**, 449 (1969); J. S. Wright and L. Salem, *Chem. Commun.*, 1370 (1969). (c) R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971). (d) N. L. Bauld and J. Cessac, *ibid.*, **99**, 942 (1977). (e) D. Cremer, *ibid.*, **99**, 1307 (1977). (f) N. L. Bauld, J. Cessac, and R. L. Holloway, *ibid.*, **99**, 8140 (1977).
- (8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
- (9) Actually, Table I shows that the energy of the π orbital ($1a_{2u}$ in I) decreases slightly upon puckering.
- (10) (a) 1,3-(CH₂)₂(BH)₂, K. Krogh-Jespersen, D. Cremer, J. D. Dill, P. v. R. Schleyer, and J. A. Pople, manuscript in preparation; (b) $B_4H_4^{2+}$, ref 3c.
- (11) RHF/STO-3G structures and energies. (a) $C_4F_4^{2+}$ (V): $R(C-C) = 1.481$ Å (opt), $R(C-F) = 1.284$ Å (opt), $E = -540.94231$ au. (b) $C_4(CH_3)_4^{2+}$ (III), C_{4v} assumed carbon skeleton planar; $R(C_{\text{ring}}-C_{\text{ring}}) = 1.467$ Å (opt), $R(C_{\text{ring}}-CH_3) = 1.507$ Å (opt) (CH_3 standard), $E = -305.58236$ au (compare $E = -305.58238$ au given in ref 3b for the C_{4h} conformation). (c) $C_4(CH_3)_4^{2+}$ (IV, C_{2v} assumed, obtained by allowing III to pucker): $R(C_{\text{ring}}-C_{\text{ring}}) = 1.459$ Å, $R(C_{\text{ring}}-CH_3) = 1.507$ Å, $\alpha = 2.18^\circ$ (axial), $q = 0.230$ Å (CH_3 standard), dihedral angle between the CCC ring planes = 154.6° , $E = -305.58602$ au.
- (12) The 1,2-dimethyl-3,4-dibenzyl or 1,2-dimethyl-3,4-diisopropylcyclobutadiene dications might be suitable for this purpose by using NMR methods.
- (13) We also considered the possibility that cyclobutadiene might have a non-planar carbon skeleton; however, such distortions produced no energy lowering in the triplet. The degenerate LUMO's of I, which are strongly destabilized in the puckered conformation (II), are both singly occupied in triplet cyclobutadiene.
- (14) The performance of the theory at levels used in this paper can be assessed by comparing the results on C_4 hydrocarbons with experiment (W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975)).

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Acarnidines, Novel Antiviral and Antimicrobial Compounds from the Sponge *Acarnus erithacus* (de Laubenfels)

Sir:

Extracts of the red-orange sponge *Acarnus erithacus* (de Laubenfels)^{1,2} from the Gulf of California have significant activity against *Herpes simplex* type 1,^{3a} as well as against *Bacillus subtilis*,^{3b} and *Penicillium atrovenerum*.^{3b} We have followed these activities during fractionation and wish to report here the structures of a closely related group of compounds, the $C_{12:0}$, $C_{12:1}$, and $C_{14:3}$ acarnidines (**1a-c**), isolated from the extracts, which possess the biological activities noted above as well as activity against other microorganisms.^{3c} The acarnidines have in common the unique substituted homospermidine skeleton shown (**1**) and differ in the fatty acid substituent R.

The acarnidines were isolated by extracting homogenized sponge with toluene-methanol (1:3) and partitioning with 1 N sodium nitrate solution.⁴ The antimicrobially active components,⁵ which were present in the aqueous phase, were extracted into chloroform and chromatographed on Sephadex LH-20 (methanol) and silica gel ($CHCl_3$ - CH_3OH -concentrated NH_3 , 6:3:1) to give **1** in 0.2% yield, essentially free of impurities. Field desorption mass spectrometry (FDMS)⁶ of the oily mixture showed the most intense M + H ions at m/e 464 (**1b**), 466 (**1a**), and 488 (**1c**).